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THE OPTICAL CONSTANTS OF PbS AS A FUNCTION OF TEMPERATURE

Mr. D. G. Avery, Telecommunications Research Establishment, Great Malvern, England, has extended his earlier measurements on the optical properties of PbS, PbSe, and PbTe (ESN 6, 216 (1952)) to cover the variation of the optical constants with temperature. The changes in optical constants which were observed are relatively small effects, and it was thus necessary to impose rather stringent requirements on the size and flatness of the specimens. For this reason, the work had to be limited to PbS; i.e. to several natural galena crystals (n-type) and to one synthetic p-type crystal. The optical techniques employed are the same as those previously described; however, in the present arrangement the specimen could be heated by means of a small heating coil in the specimen holder. The temperature range covered was from 10° - 350°C.

The specimen was kept in a vacuum at 10^{-4}mm Hg, and it was found that all variations in the optical constants as a function of temperature were reversible, i.e. that the changes disappeared on returning to room temperature. If the specimen was kept in an atmosphere of oxygen at several millimeters Hg, permanent changes in the optical constants were introduced at temperatures above 200°C.

The most striking result of the effect of temperature on the optical constants is that the characteristic long wavelength tail of the absorption band (in the range λ = 1 to 3.1μ) progressively vanishes as the temperature

is raised. Further, the measurements show that the position of the absorption edge (0.4 ev at room temperature) shifts toward shorter wavelengths at about 4×10^{-4} ev/°C up to temperatures of about 125°C in agreement with the recent results of Paul, Jones and Jones (Proc. Phys. Soc. 66B, 194 (1953)). At temperatures higher than this, however, the rate of change of the edge position becomes greater.

Measurements were also made on the temperature dependence of the long wavelength ($> 3\ \mu$) refractive index of PbS. The experimentally observed value is $-(5.5 \pm 1.5) \times 10^{-4}$/°C. The variation of the refractive index, n, can also be computed from Moss's relationship between the refractive index and the spectral limit of photoconductivity, λ_c, (Proc. Phys. Soc. 64A, 590 (1951)). In Moss's equation, $n^4 = C\lambda_c$, where C is a constant. Further, assuming the photoconductive threshold λ_c is the same as the absorption edge E, one obtains $dn/dT = -(n/4E)dE/dT$. Putting $n = 4$, $E = 0.4$ ev, and $dE/dT = 4 \times 10^{-4}$ ev/°C, one obtains $dn/dT = -10^{-3}$/°C. This result compares favorably with the experimental value.

TEMPERATURE VARIATION OF THE DRIFT MOBILITY OF HOLES

Mr. R. Lawrence of the Telecommunications Research Establishment, Great Malvern, England, has recently measured the drift mobility of holes in n-type germanium single crystals as a function of temperature in the range 100° - 360° K. The experimental arrangement was the same as that described by Lawrence and Gibson (Proc. Phys. Soc. B65, 994 (1952)) with the addition of a small micromanipulator for use at low temperatures, which was designed by W. H. Mitchell of TRE. This apparatus consisted of a small two-carriage micromanipulator encased in a vacuum-tight glass Dewar vessel.

As the temperature was lowered the drift mobility increased steadily to a certain point, and then was observed to decrease rapidly (see accompanying figure). The decrease in mobility was attributed to trapping of the holes, and subsequent observations verified this. The traps are believed to be on the surface and about 0.11 ev deep. Steady illumination of the specimen with light from a tungsten lamp was found to eliminate the effects of trapping completely. In this way it was possible to measure the temperature variation of the hole mobility, due to lattice scattering, below the temperature at which trapping normally set in. In

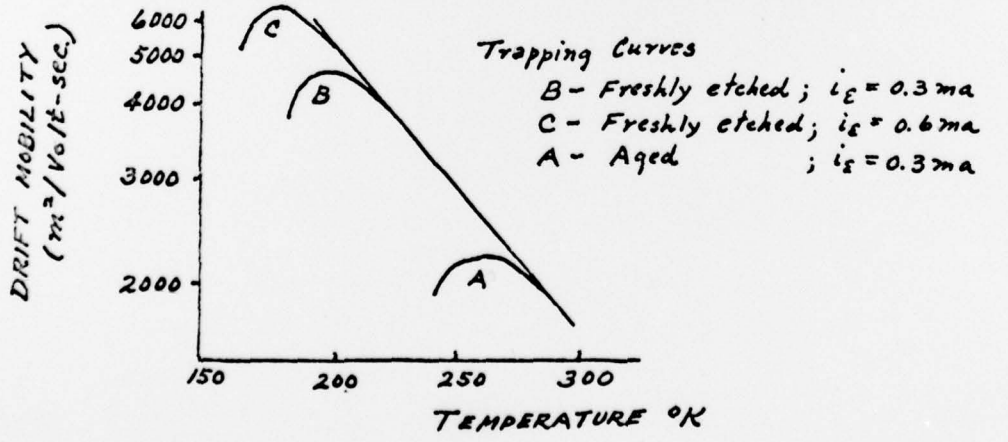
the temperature range investigated, it was found that the drift mobility varied as $T^{-2.3}$, not in accordance with the theoretical relationship of $T^{-3/2}$; these results thus agree with the Hall mobility of holes in p-type germanium as given by Dunlap (Phys. Rev. 79, 286 (1950)). The mobility of electrons in n-type germanium essentially follows the theoretical relationship.

At low temperatures a hole will spend more of its time in the vicinity of a trap, the trapping time increasing according to $t_t = S^{-1}\exp(E/kT)$, where E is the trap depth, and S the relaxation frequency of the trap. If τ is the average time the hole spends in the full band between captures, and μ_o is the drift mobility of holes in the absence of trapping, then the effective mobility is given by

$$\mu_{eff} = \mu_o \tau/(\tau + t_t) = \mu_o/(1 + S^{-1}\tau^{-1}\exp(E/kT)).$$

The average time, τ, spent in the full band between the captures is dependent on the number of traps present; thus τ will be only a slight function of temperature and may be treated as a constant provided the sweeping field and the emitter current are kept constant as the temperature is lowered. The above equation was used to determine the trap depth, 0.11 ev, from the experimentally determined mobility curves in the region of trapping. When trapping set in, it was also observed that the shape of the hole pulse, upon arrival at the collector, had changed shape considerably.

The above experiments were performed in vacuum. Upon initial evacuation it was found that the collector efficiency fell considerably, and this effect was attributed



to the removal of water vapor from the surface of the germanium. Further experiments have substantiated this hypothesis.

A NEW METHOD FOR THE DETERMINATION OF SHORT HALFLIVES OF ISOMERS

Dr. O. Bruna and Dr. F. Dinhobel of the Second Physical Institute of the University of Vienna have recently developed a method for the measurement of half-lives of less than one second, for isomers produced through (n,γ) reactions. The principle of the method consists of activating the sample by means of a periodically interrupted neutron beam; this produces a periodic rise and decay of the gamma-ray activity which is measured by means of a counter.

Neutrons from a radium-beryllium source are thermalized by means of paraffin and concentrated by means of a paraffin rod. An effort is made to remove most of the gamma rays of the source by absorption in lead. The neutrons pass through a steel disk near its periphery, the disk having two 90° cadmium sectors located opposite each other. Finally the neutrons hit the material to be activated which is mounted in front of the counter. When the disk is rotated, the neutrons which are practically not absorbed by the iron produce an increasing activity of the sample until the cadmium sector enters the neutron beam, when the activity again decreases. The activity curve can be obtained by photographing the output of the counter scaling circuit continuously, but the Vienna scientists have instead chosen a method for determining the activity curve point-by-point, by turning on the scaling circuit only at particular points of the curve. They do this by mounting on the axis of the steel disk a drum, on the periphery of which are two conducting sectors each 10° wide and 180° apart. A sliding contact serves to turn the scaling circuit on and off. This drum can be turned with respect to the cadmium sectors so that the activity of the sample can be determined at any point of the activity curve.

The accuracy of the method depends mainly on the intensity ratio of the activity to background, and the background is due mostly to gamma rays from the neutron source. It was found that at a certain distance from the source an optimum condition exists since the neutron intensity up to this distance falls off approximately as

$1/r$, while the gamma ray intensity falls off as $1/r^2$. The greatest part of the background at this position, approximately 90 per cent, still comes from the radium-beryllium source. The rest comes from cosmic rays and from the gamma rays produced by neutron capture in cadmium. A further decrease of sensitivity comes about because of the finite size of the sample, so that the activation does not begin in all of its parts at the same time. The maximum phase difference is given in terms of the width of the sample and the peripheral velocity of the steel disk. The useful part of the activation curve or decay curve is therefore only $90-\alpha^{\circ}$, where α is the width of the sample in degrees.

The sensitivity of the method could be increased considerably by using a gamma-free neutron source, for example, a polonium-beryllium source or neutrons from a D-D reaction.

The shortest measurable halflife is determined by the maximum rotational velocity of the steel disk and lies at about 2×10^{-4} seconds. The complete method using this arrangement has been tested on two emitters of known halflife (silver and indium) and has given results in good accord with other methods.

PENTAALKYL COMPOUNDS OF THE FIFTH GROUP ELEMENTS

The methods developed by Professor G. Wittig (Tübingen) for the preparation of the pentaphenyl derivatives of the fifth group elements: phosphorus, arsenic, antimony, and bismuth, have recently been extended to analogous alkyl compounds. Pentamethyl antimony has been prepared, and the synthesis of pentamethyl arsenic appears feasible on the basis of exploratory experiments.

The reaction

$$\left[R_4P\right] X + RLi \longrightarrow R_5P + LiX$$

is the general method used to prepare these interesting compounds. Here R is the aryl or alkyl radical, X is halogen, usually chlorine, and the reaction is performed in anhydrous ether, under rigorous exclusion of oxygen, sometimes at low temperatures.

Pentamethyl antimony is a colorless, poisonous, liquid with a boiling point of 126°C/730mm. It is a homopolar compound, similar to the previously reported penta-

phenyl compounds and to the mixed aryl-alkyl compound, tetraphenyl-trityl-phosphorus (cf. Wittig et al., Ann., 580, 44 (1953); 578, 136 (1952); 577, 26 (1952)).

INTERMOLECULAR FORCES AND THE APPLICATION OF RAMAN SPECTROSCOPY TO QUANTITATIVE ANALYSIS

Some recent results obtained by Professor J. Goubeau (Stuttgart) underline the necessity for considering in more detail the effect of intermolecular forces on the intensity of Raman lines. This effect may seriously interfere with the precision of quantitative analysis based on the intensity of Raman lines in liquid mixtures. The system under study was the benzene-cyclohexane mixture, and the result may also be of value in a further understanding of the "structure" of such mixtures. The technique used was to make a direct comparison between the intensity of the very strong breathing frequency of benzene resulting from scattering by the same number of benzene molecules in (a) pure benzene, and in (b) benzene-cyclohexane mixtures of various composition. The results indicate that the intensity of this Raman line per benzene molecule begins to decrease measurably at 2°/o cyclohexane concentration and continues to decrease until 50°/o cyclohexane concentration. From this point onward it has a constant value which corresponds to about 70°/o of that in pure benzene. These results are undoubtedly connected with the well known decrease in the "order" of liquid benzene upon dilution with cyclohexane. The results were also analyzed throughout the entire concentration range in terms of the intensity of a suitable Raman line of the second component, cyclohexane. The fact that this behaves normally, i.e. that the observed intensity is precisely proportional to the total number of scattering units, indicates the reliability of the results.

It may be concluded that precise studies of this type will be needed before Raman intensities can be used to estimate concentrations reliably, without direct comparison with "standard" mixtures.

HIGH TEMPERATURE RAMAN SPECTRA OF FUSED SALTS

Raman spectra of fused salts at high temperatures are being investigated in the laboratory of Professor J. Goubeau (Stuttgart). A graphite vessel is used to contain the fused salts, the container being surrounded by an outer housing. A high pressure mercury light source, together with a suitably arranged mirror, are fitted to the

inside of the top of the outer housing and the scattered light emerges through a small window. The angle between the incident light and the observed scattered light is about 20°. Satisfactory Raman spectra have been obtained up to 600°C with 36-hour exposures, and it is hoped to extend the measurements up to 1000°C.

The results obtained on fused lithium nitrate indicate that the symmetry of the nitrate ion is distorted under these conditions. It is believed that complex ions such as

$$\left[Li_2NO_3\right]^+$$

are present in this system.

ISOSTERIC ADDITION COMPOUNDS

A series of isosteric addition compounds was [illegible]ly prepared by Professor J. Goubeau (Stuttgart). [illegible]parent molecule, $(CH_3)_3N{\cdot}BCl_3$, is well known; the new compounds are 1:1 adducts of trimethylamine with phosgene, $COCl_2$, and with nitrosylchloride, NO_2Cl. All of these have the same number of bonding electrons.

The stability of the phosgene adduct is very much lower than that of the borontrichloride one, while the nitrosylchloride compound is intermediate in stability. It thus appears that the explanation advanced for the great decrease in stability on replacing BCl_3 with $COCl_2$, i.e. the presence of a semipolar bond in the $COCl_2$ molecule, is not entirely satisfactory (cf. Z. anorg. allg. Chem. 271, 235 (1953)).

HUME-ROTHERY PHASES IN TERNARY SYSTEMS

Professor F. Mazzoleni of the University of Rome is investigating the existence of structurally analogous phases in ternary systems. This problem has scarcely been investigated previously, and his research represents the only study of the problem. In a previously published paper, Accademia Nazionale Dei Lincei, 9, December (1951), Mazzoleni outlined a general theoretical approach to the formation of Hume-Rothery phases in systems containing more than two components. Predictions were made of the composition of structurally analogous phases for the various electron-atom ratios for ternary, quaternary, and quinternary systems.

For the case of a ternary system Mazzoleni predicted the following compounds, where A is a zero valent transition element, B is a monovalent metal, and E is a tetravalent metal.

Electron-Atom Ratio	Compound		
3:2	$A\,B_2E$	$A_3B\,E_2$	
21:13	$A\,B_9E_3$	$A_4B_5E_4$	$A_7B\,E_5$
7:4	$A_3B_2E_3$	$A_6B\,E_5$	

These predictions have now been put to tests by experiments using Ni (A), Cu (B), and Sn (E). All of the above compounds have been prepared and their crystal structure determined by X-ray diffraction. In each case Mazzoleni has found that the phase has the crystal structure analogous to that for the indicated electron-atom ratio. Thus the compounds with 3:2 electron-atom ratio have the body centered cubic beta structure; those with the 21:13 electron-atom ratio have the complex cubic gamma-brass structure; and those with the 7:4 ratio have the close-packed hexagonal structure of epsilon-brass. Mazzoleni expects to publish this work in La Metallurgica Italiana.

In the preparation of specimens for metallographic examination, it was qualitatively observed that these ternary Hume-Rothery phases have high corrosion resistance. In all cases aqua regia was required for etching. While these phases themselves probably have little practical importance as corrosion resistant materials, a study of their chemical behavior may be of importance to the theory of corrosion.

GÖTTINGEN DIGITAL COMPUTER COLLOQUIUM

A colloquium on digital computers was held at Göttingen, 19-21 March 1953. This meeting was sponsored by the Computer Committee of the German mechanics society (Gesellschaft für angewandte Mathematik und Mechanik, GaMM), of which Professor E. Kamke of the University of Tübingen is now the chairman. The principal item of news in this meeting was the announcement of the specifications for the projected Munich computer, being developed by Professor H. Piloty with the cooperation of the mathematician Professor R. Sauer.

The Munich computer is to be developed on a building block principle in order to facilitate manufacture and will be of the binary parallel type. It will

be based on a floating binary point, with negative numbers handled through the use of complements. The arithmetic unit will be composed of about 550 tubes and will handle numbers of about 40 binary digits.

The storage is to consist of a magnetic drum, 10 cm in diameter by 20 cm long, running at 15,000 rpm. The drum will have 200 tracks, each with 2000 binary digits, permitting the storage of 8000 numbers of 50 binary digits each. Work is progressing on the development of the various elements to be used in the computer.

The state of German digital computer progress as indicated by this meeting is reported in Technical Report CNRL-75-53, available from the Technical Publications Office, Code 740, ONR, Washington 25, D.C.

THE ANNUAL MEETING OF GaMM

The annual meeting of GaMM, the German mechanics society, was held on 21-25 April 1953 in Aachen. The meeting is reported in Technical Report, ONRL-76-53, and two of the contributions, by Stiefel and Schäfke, are presented briefly below.

A Quotient-Difference Procedure for Eigenvalue Problems

A procedure has been found by Professor E. Stiefel of the E.T.H. in Zürich for the numerical treatment of a set of Schwarz constants for a symmetric (or Hermitian) operator. The procedure yields successive sets of constants which are related in the following manner: the quotients of consecutive constants in the (n)th set are calculated, and the differences of these quotients obtained; these differences are corrected by the addition of the corrected differences obtained in the calculation for the (n-1)th step; the constants multiplied by the corrected differences then yield the (n+1)th set of constants. The significance of the procedure comes from the following specific properties: if the eigenvalues of the operator are all positive real and distinct, then the ith set of quotients is a series which approaches the ith largest eigenvalue. If the total number of eigenvalues is finite and equal to n then the nth differences in the process vanish.

An accompanying procedure was found by Professor Stiefel which gives, in the case of a finite number of eigenvalues n, the characteristic polynomial after n steps.

More complete details of these procedures are given in ONRL-76-53.

Stability Criteria for Hill's Equation

Dr. F. W. Schäfke of the University of Mainz presented two sets of stability criteria for Hill's equation which are the best possible ones of their particular type. If Hill's equation is expressed

$$\ddot{y} + f(t)y = 0 ,$$

where $f(t)$ is periodic of period π, Schäfke's criteria for stability are

$$K_1 \begin{cases} \alpha^2 \leq f(t) \\ (n-1)^2 \leq \alpha^2 < n^2 \\ \frac{1}{\pi}\int_0^{\pi} f(t)\,dt \leq \alpha^2 + \frac{2n\alpha}{\pi}\cot\frac{\pi\alpha}{2n} \end{cases}$$

or

$$K_2 \begin{cases} f(t) \leq \alpha^2 \\ n^2 < \alpha^2 \leq (n+1)^2 \\ \frac{1}{\pi}\int_0^{\pi} f(t)\,dt \geq n\alpha \end{cases}$$

These criteria include several formerly derived as special cases, and are discussed more fully in ONRL-76-53.

NEW TECHNIQUE FOR THE MICROSCOPIC EXAMINATION OF FINE PARTICLES

Dr. R.G.H.B. Boddy of the Medical Research Council Pneumoconiosis Research Unit, Cardiff, has devised a new technique for the microscopic examination of fine particles. Small particles of many substances when squeezed between two glass plates spread and become thin. A crushing condenser has been designed so that the process can be watched with the microscope. Measurements of the particles and observations on the manner and results of crushing afford new information about them. The technique is particularly

applicable to such materials as coal, opaque under normal circumstances, but translucent when thin. The samples for crushing are prepared by the "delta" settling technique, which consists of drawing a steady air-stream containing suspended dust particles through a low horizontal duct. The larger particles are removed by gravity settling. The "delta" apparatus is arranged so that the deposition of dust upon a sample slide can be watched through the microscope and an adequately sized and distributed sample obtained.

A STUDY OF THE CHOROIDAL CIRCULATION OF THE EYE IN MAN

K. C. Wybar of the Institute of Ophthalmology, London, has studied the choroidal circulation in the human eye by intravascular injection of Neoprene latex. He has found that the choroid is supplied by two arterial systems. The first system is composed of the short posterior ciliary arteries which divide into many branches as they pierce the sclera around the optic nerve and terminate in arterioles which open into the chorio-capillaris. Each branch confines its arteriolar-capillary network to a localized zone of the choroid between the optic disc and the equator of the eye. The second system is composed of recurrent choroidal arteries which arise from the long posterior ciliary arteries, from the anterior ciliary arteries and from the major arterial circle of the iris, and which supply the anterior part of the choroid meeting the short posterior ciliary arteries near the equator. The junction of the two arterial systems may be marked by an intervening capillary network, but it is not uncommon for a direct branch to effect the union and in certain cases the vessels may inosculate.

The capillaries in the anterior part of the chorio-capillaris are larger than those in the posterior part, and the intercapillary meshwork is more open anteriorly. There is no evidence of any arterio-venous anastomoses in the choroid.

IMPROVED ACCURACY IN MEASURING LOW LEVELS OF PERCENTAGE OXYGEN SATURATION

Professor F.J.W. Roughton of the Department of Colloid Science, Cambridge University, has developed a method for improving the accuracy of the oxygen determinations when the percentage of oxygen saturation of the blood is low. It is found under these circumstances that the ordinary treatment of the blood with ferricyanide

removes only about 85°/o of the bound oxygen. The residual amount of oxygen becomes less and less important as the oxygen content of the blood increases. However, for accuracy at low levels of oxygen saturation, this error is increasingly significant. A successful method of attack on this problem is to treat the oxygenated blood with carbon monoxide. The carbon monoxide completely replaces the oxygen from the hemoglobin. The blood so treated can be analyzed for total combining capacity with carbon monoxide and therefore with oxygen. The oxygen and carbon monoxide mixture after the replacement can be analyzed in the Van Slyke apparatus for the amount of oxygen. The latter determination will provide an accurate measure of the oxygen bound at low concentration and with the former measurement will give an accurate estimate of the percentage of oxygen saturation.

Further information about the research in progress at the Department of Colloid Science, Cambridge, can be obtained from Technical Report CNRL-77-53, available from the Technical Information Office, Code 740, Office of Naval Research, Washington 25, D.C.

THE CASE OF THE "MISSING FUNDAMENTAL"

The University Clinic for Diseases of the Ear, Nose and Throat, Utrecht, is carrying on a program of research in the general areas of hearing and equilibrium. Its director, Professor A.A.J. van Egmond, is the 1953 recipient of the Barany medal which was presented to him in testimony to the work of the Clinic research staff.

An interesting research being conducted by Dr. G. A. Hoogland is concerned with the "case of the missing fundamental", which occurs when the pitch of a complex tone is judged to be that of a difference tone. For example, when tones of 400, 500, and 600 cycles are presented, the pitch of the complex tone is judged to be 100 cycles, the value of the difference tone. Since the 100 cycle tone is not present in the stimulus, it has been attributed by certain researchers to the stimulating effect of the recurrent envelope of frequencies - a conclusion that might speak against a "place theory" of audition. For example, it is possible to consider that at low frequencies only a single component of the complex wave acts on the cochlea resonators, but that, at higher frequencies, several components affect the resonators. At the high frequencies the several components may beat together, and it may be postulated that it is the beat that maintains the periodicity at the basic fundamental frequency. The elimination of low

frequency components should have no effect upon this periodicity.

Hoogland tested this idea by using a subject in whom the high frequency components were not registered. A person was found who had an audiogram showing a sharp cut-off in both ears at about 1000 cycles per second. Five loud speakers were used to give the auditory stimulus, each one giving a pure tone. Despite the fact that the subject could not hear the higher frequencies presented by the stimuli he nevertheless heard a tone at 100 cycles. Thus, the results of the experiment very clearly do not support the "envelope" hypothesis. The Utrecht investigator concludes that the perception of the 100 cycle pitch is due to a shift of energy by nonlinear processes to the 100 cycle frequency.

Further results of research on vision and hearing, supported by the National Defence Research Council of the Netherlands (TNO), are described in Technical Report CNRL-80-53, available from the Technical Publications Office, Code 740, Office of Naval Research, Washington 25, D.C.

TECHNICAL REPORTS OF CNRL

The following reports have been forwarded to ONR, Washington, since the last issue of ESN. Copies may be obtained from the Technical Publications Office, Code 740, Office of Naval Research, Washington 25, D.C.

CNRL-63-53 "Solutions of Electrolytes in Organic Solvents" by R. W. Mooney

CNRL-64-53 "Symposium on Automatic Digital Computation at the National Physical Laboratory" by R. R. Weber

CNRL-67-53 "Nuffield Research Unit Into Problems of Ageing, Cambridge" by C. H. Graham

CNRL-68-53 "Some Recent Researches of the Applied Psychology Unit, Cambridge" by C. H. Graham

CNRL-69-53 "An Improved Gravimeter" by W. L. Hyde

CNRL-70-53 "The Nottingham Meeting of the Experimental Psychology Group" by C. H. Graham

CNRL-71-53 "Colloquium on Optical Problems of Vision, Madrid" by C. H. Graham

CNRL-72-53 "Meeting of the Medical Research Society, London, 1 May 1953" by J. L. Tullis

CNRL-74-53 "Recent Research on Angular Correlations at the E.T.H., Zurich" by J. K. Beling

CNRL-75-53 "A Second Progress Report on German Computer Work" by W. D. Hayes

PERSONAL NEWS ITEMS

Professor Sir Eric Rideal will shortly become Chairman of the Minister's Advisory Council on Scientific Research and Technical Development in succession to Professor Sir John Lennard-Jones. Professor Rideal, who is Professor of Physical Chemistry at King's College, London, has been associated with the research work of the Ministry of Supply since the early part of last year.

The Ministry of Supply has also announced the following appointments to the Minister's Advisory Council: H. W. Melville (Professor of Chemistry, University of Birmingham), J.L.M. Morrison (Professor of Mechanical Engineering, Bristol University), L. Rosenhead (Professor of Applied Mathematics, Liverpool University), I. N. Sneddon (Professor of Mathematics, North Staffordshire University College), and A. R. Todd (Professor of Organic Chemistry, Cambridge University).

FORTHCOMING EVENTS

A joint meeting of the German Physical Society and the Austrian Physical Society will be held at Innsbruck, Austria, on 20 - 24 September 1953.

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